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ROBUSTNESS AND STABILITY OF JET-COOLED ALPHA-METHYL STYRENE

by

V. M. Kargin, E. P. Borsteln, J. J. Seeman

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SPECTROSCOPY AND STRUCTURE OF JET-COOLED ALPHA-METHYLSTYRENE

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ABSTRACT

The sterically hindered styrene derivative, α -methylstyrene (2-phenylpropane), is studied by 1-color time-of-flight mass spectroscopy (TOFMS). In contrast to styrene, which has an intense spectral origin transition in the TOFMS, α -methyl styrene exhibits a weak origin transition. A progression in a low frequency torsional mode, with an energy level spacing of $69/\text{cm}^{-1}$, is built on the origin. The intensity maximum of this progression occurs at the eighth peak position, indicating that the ground and excited state geometries are displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of 32 cm^{-1} in the ground state. Potential parameters derived from an analysis of the spectra are $V_2 = 0.0$ and $V_4 = 150.0\text{ cm}^{-1}$ for S_0 and $V_2 = 4867$, $V_4 = -500$ and $V_6 = -80\text{ cm}^{-1}$ for S_1 . In the ground state the propenyl group is calculated to be at a 31° angle from the plane of the aromatic ring. Analysis of the Franck-Condon intensity profile yields a displacement in the excited state, for the angle between the aromatic and ethylenic groups, of 30° relative to the ground state. α -methylstyrene is suggested to be nearly planar in its first excited $\pi-\pi^*$ state.

I. INTRODUCTION

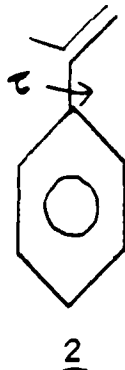
Styrene (phenylethylene) (1) has been the subject of numerous experimental and theoretical studies.¹⁻⁷ The reasons for the intense interest in styrene are many: styrene is structurally related to stilbene, a prototypical 1,2-disubstituted ethylene which can undergo photochemical cis \rightleftharpoons trans isomerization; and styrene is also an important reactant for organic synthesis, notably in polymer chemistry.



It has been established that conjugation between the two π systems (olefinic and aromatic) is important in this molecule as is evidenced by the planar conformation of styrene in both the ground (S_0) and first excited state (S_1).^{3,6} Conjugation between the two (olefinic and aromatic) π systems of styrene and its derivatives has important consequences for the photochemistry and photophysics for this class of molecules. Recently, using supersonic molecular jet spectroscopy we have shown that styrene derivatives which are not sterically hindered also have planar conformations in both S_0 and S_1 .⁸ The molecules studied by this technique include trans- β -methylstyrene, 3-methylstyrene, 4-ethylstyrene and 4-methoxy-trans- β -methylstyrene.

This present work extends these supersonic jet spectroscopic studies to sterically hindered molecules. α -methylstyrene (AMS) (2) is such a molecule in which the bulkier methyl substituent has replaced the α -hydrogen atom on the vinyl group. The alpha-methyl/ortho-hydrogen steric interaction is large enough to cause a non-planar conformation of this molecule in the

ground state. The non-planarity of AMS in the ground state has been postulated from the decrease in λ_{\max} relative to that of styrene for the $\pi-\pi^*$ ($S_1 \leftarrow S_0$) transition of AMS in solution.⁴ The deviation from planarity (as defined by the angle τ) for AMS has been estimated to be 33° in S_0 based on solution phase absorption data.⁴ The conformation of this molecule in the excited state is, as yet, unknown.



Supersonic molecular jet spectroscopy is ideally suited for the conformational studies of sterically hindered styrenes. The rotationally and vibrationally cooled molecules produced in the expansion exhibit uncongested spectra relative to room temperature gas phase spectra.⁹ If a displacement in the torsional angle τ occurs in the excited state a progression in the spectral features associated with the torsional motion will be observed in the excitation spectrum. The extent of such a change upon excitation can be calculated from a Franck-Condon intensity analysis of this torsional progression. This type of torsional analysis for non-rigid systems cooled in a supersonic jet expansion has been successfully applied to biphenyl,¹⁰ 9-phenylanthracene,¹¹ and 9-(2-naphthyl)-anthracene.¹²

II. EXPERIMENTAL

The supersonic jet expansion as well as the time-of-flight mass spectrometer have been described previously and we refer the reader to reference 13 for details on the experimental apparatus. Briefly, the supersonic

expansion is generated using a pulsed R.M. Jordon valve. Helium is used as the carrier gas at a pressure of 3-4 atm. Argon is used for the carrier gas in determining the spectroscopic origin so as to eliminate any hot-bands in that region. A tunable pulsed dye laser, which is pumped by the second harmonic (532 nm) of a Nd:YAG laser, is frequency doubled and focused with a 1 meter quartz lens into the vacuum chamber. Fluorescein dye is used in all of these experiments. The ions are produced by sequential photon absorption and are accelerated into the flight tube where they are detected by a microchannel plate.

AMS was purchased from Aldrich and used without further purification. All compounds are stored in the dark at 4°C to prevent polymeriaztion.

Synthesis of d₅-AMS:

III. RESULTS

The time-of-flight mass spectrum of AMS is shown in Figure 1. The spectrum was scanned from the origin, 0₀⁰ transition, to 1500 cm⁻¹ higher in energy. A progression in a low frequency mode built on the origin is clearly visible in the spectrum. The average spacing of this progression is ~69 cm⁻¹. Table I lists the frequencies of the progression as well as the spacings between each energy level. The spacings between the energy levels become larger at higher levels. This negative anharmonicity suggests that the potential energy surface for this motion in the excited state, is flat near the equilibrium angle but has steeply rising walls. This low frequency motion is also built on other spectral features, i.e. higher vibrational modes.

The origin region is shown in an expanded scale in Figure 2. Both pure

argon and pure helium was used as the carrier gases in determining the position of the spectral origin so as to eliminate any hot bands in the spectrum. The lowest energy peak at 35063.7 cm^{-1} is assigned to the spectral origin, i.e. the 0_0^0 transition (Table II).

The TOFMS of d_5 -AMS (deuterated propenyl group) is shown in Figure 3, recorded from 35000 to 36000 cm^{-1} . Listed in Table III are the energies of the low frequency vibration and the energy level spacings for its progression for the partially deuterated compound. The average energy of this mode is reduced to $\sim 64\text{ cm}^{-1}$ upon deuteration of the propenyl group. The most intense feature in the progression occurs at the seventh peak position. The 0_0^0 transition energy is determined to be 35083.6 cm^{-1} (Table II).

Although the spectrum of AMS is quite congested, other higher frequency vibrational modes of this molecule in the excited state can be determined. One mode is observed at an energy of 369.5 cm^{-1} which shifts to 341.1 cm^{-1} in the partially deuterated compound (see Figures 1 and 3). The other peak identified as a vibrational mode occurs at 738.7 cm^{-1} for the perhydro molecule and 722.1 cm^{-1} for the d_5 -deuterated species. The energies of these vibrations are listed in Table IV. The low frequency progression is built on both of these vibrations, with an energy level spacing of approximately 69 cm^{-1} for AMS (2) in the excited state. The progression built on these two vibronic features are similar in intensity to that observed for the origin the maximum peak intensity for the progression occurs at the ninth member.

Information on this 69 cm^{-1} mode can be obtained for the ground state as well. At low backing pressures for the expansion ($<40\text{ psig He}$) hot bands appear around the origin. Figure 4 shows such spectra from which the

torsional mode energy in the ground state can be determined to be ca. 32 cm^{-1} . Clearly, however, the ground state is not as well determined as is the excited state for this mode.

IV. ANALYSIS AND DISCUSSION

A. Assignment of the Low Frequency Mode

Assignment of the low frequency mode, identified as $\sim 69 \text{ cm}^{-1}$ in S_1 and $\sim 32 \text{ cm}^{-1}$ in S_0 of AMS, can be made based on the following two considerations. First, a comparison of the AMS origin region ($0_0^0 + 200 \text{ cm}^{-1}$) with that of styrene (Figure 5). In contrast to the AMS spectrum (Figure 1), the 0_0^0 transition of styrene is intense and the origin region is devoid of any spectral features up to 200 cm^{-1} . Second, the mode undergoes a substantial shift (from 69 to 64 cm^{-1}) upon deuteration of the propenyl group. We conclude, therefore that this low frequency mode can be assigned to the torsional motion whose displacement is indicated by τ in 2.

The repulsive steric interaction between the α -methyl group and the ortho hydrogen inhibits the planarity of AMS. The potential energy surface has a minimum at some angle $\tau \neq 0$ i.e., the planar conformation is unfavorable for this sterically hindered styrene derivative in one or both of the electronic states S_0 and S_1 . A balance must be struck between conjugation and steric repulsive interactions.

A displacement along the coordinate τ occurs in the excited state, with the respect to the ground state, as is evidenced by the presence of a Franck-Condon intensity envelope for this motion in the jet-cooled excitation spectrum (measured using the TOFMS technique). The change in the angle τ can be determined from a Franck-Condon intensity analysis of the spectrum. Since such an analysis depends on accurate torsional eigenvectors for both the ground and excited states, prior to a Franck-Condon calculation the form

of the potential surface must be determined for the molecule in both S_0 and S_1 electronic states. The form of the potential and the eigenvalues and eigenvectors for the torsional motion are discussed in Section IV-C below.

B. Assignment of Higher Frequency Vibrational Modes:

Vibrational assignments for two of the higher energy modes of AMS in S_1 can be made from a comparison of the present AMS results with those for styrene² (see Table IV). The 6^1 vibration at 394.5 cm^{-1} in styrene shifts to lower frequency, 369.5 cm^{-1} (341.1 cm^{-1}), for AMS (d_5 -AMS). The 1^1 vibration in the excited state of AMS is assigned to the peak at 738.7 cm^{-1} shifted to 722.1 cm^{-1} for the partially deuterated compound. These frequencies can be compared to those of the 1^1 vibrational mode for styrene which is at 745.8 cm^{-1} .

C. Calculations of the Torsional Energy Levels and Franck-Condon Factors

A one-dimensional rotor analysis is used to fit the frequencies of the torsional mode. The general form of the potential function can be expressed as a cosine Fourier series,

$$V(\tau) = \frac{1}{2} \sum_n V_n (1 - \cos n \tau) \quad (1)$$

The Hamiltonian of the free rotor is then modified by including this potential term. The Schroedinger equation for the hindered rotor can be written as

$$\left[-B \frac{\partial^2}{\partial \tau^2} + V(\tau) \right] \psi_m(\tau) = E_m \psi_m(\tau) \quad (2),$$

in which B is the reduced rotational constant for the internal torsional mode. Free rotor wavefunctions are used as a basis set. A total of 109 basis functions are needed to ensure convergence of all the energy levels. The best fit to the excited state data using equation (2) is obtained with the following parameters: $V_2 = 4867.0$, $V_4 = -500.0$, $V_6 = -80.0 \text{ cm}^{-1}$ and $B = 0.444 \text{ cm}^{-1}$ ($B = 0.387 \text{ cm}^{-1}$ for d_5 -AMS). The inclusion of a V_6 term is necessary to

reproduce the large negative anharmonicity in the energy level spacings (see Tables I and III). Table V lists the observed and calculated energy level values; the two are in good agreement for both AMS and d_5 -AMS.

The form of the ground state potential should differ somewhat from that of the excited state. We assume that the ground state potential should have maxima at $\tau=0$ and $\tau=90$ degrees. The reason for the potential being a maximum at $\tau=0^\circ$ has already been discussed and is attributed to the steric interaction between the α -methyl group and the orthohydrogen. The complete loss of resonance stabilization between the aromatic and ethylenic π systems at $\tau=90^\circ$ causes the potential to be a maximum at this angle also. The dominant term in the potential function will then be a V_4 term with maxima at 0, 90, 180 and 270 degrees.

Employing a potential for the ground state torsional motion with a dominant V_4 term and a small V_2 term, we find $V_2 = 0.0 \text{ cm}^{-1}$ and $V_4 = 150.0 \text{ cm}^{-1}$ ($B = 0.444 \text{ cm}^{-1}$) for the best fit to the ca. 32 cm^{-1} observed ground state torsional mode.

The displacement of the torsional coordinate in the excited state with respect to its ground state equilibrium position can be determined by a Franck-Condon intensity analysis of the torsional progression. The eigenvectors for the torsional motion can be written as $\psi_g(\tau)$ and $\psi_e(\tau+\Delta\tau)$ for the ground and excited states, respectively. The Franck Condon factors for transitions from the lowest level in the ground state potential well (zero point level) to the torsional levels of the excited state potential surface can be written as

$$\langle \psi_e(\tau+\Delta\tau) | \psi_g(\tau) \rangle \quad (3)$$

$$= \langle \sum_m c_m^e \psi_m(\tau+\Delta\tau) | \sum_m c_m^g \phi_m(\tau) \rangle \quad (4)$$

$$= \langle \sum_m c_m^e c_m^g \langle \psi_m(\tau+\Delta\tau) | \phi_m(\tau) \rangle \rangle \quad (5)$$

$$= \sum_m c_m^e c_m^g \cos m(\Delta\tau) \quad (6)$$

$$m = 0, \pm 1, \pm 2, \pm 3 \dots$$

These Franck-Condon calculations give a displacement angle calculated to be equal to $30 \pm 5^\circ$ for an intensity pattern in which the eighth peak position is a maximum. The uncertainty in the displacement angle is caused by two factors: the approximate form of the ground state potential and the uncertainty in the maximum intensity peak position (8 ± 1).

D. Determination of the Equilibrium Value of τ in the Ground and Excited States.

The analysis presented above demonstrates that the equilibrium torsional angle τ is not the same in the ground state and excited states of AMS. Only the displacement of τ , $\Delta\tau$, between the two states is known. The values of the equilibrium position for τ in the two states are, however, yet to be determined. The relationship between the geometry of molecules and their electronic absorption spectra has been discussed by Suzuki.⁴ We follow the molecular orbital theory approach developed and employed by Suzuki to determine the ground state geometry of AMS in solution, and apply it to the gas phase supersonic jet data.

The resonance energy associated with the interaction between the aromatic and ethylenic π systems of styrene is at a maximum at $\tau = 0^\circ$ and a minimum at $\tau = 90^\circ$. The energy of the electronic transition increases as τ increases from 0 to 90° . In the limit of $\tau = 90^\circ$ the two π systems are orthogonal to each other and the electronic absorption spectrum, in particular the 0_0^0 transition energy, should be similar to that of of an alkylbenzene. In the limit of maximum resonance energy ($\tau = 0^\circ$) the electronic transition energy will be similar to that found for sterically unhindered substituted styrenes, such as *trans*- β -methylstyrene which is known to be planar.⁸

These transition energies have been calculated⁴ using Hückel theory for the planar and perpendicular limits. The analysis considers only a one electron transition and neglects relaxation effects. The calculated transition energy and the experimentally determined energy are assumed to be linearly related in this treatment. The transition energy for $0^\circ < \tau < 90^\circ$ can be calculated from the equation,

$$\Delta E = \Delta E_{\tau=90} - \frac{(\Delta E_{\tau=90} - \Delta E_{\tau=0}) (\nu_{\tau=90} - \nu)}{(\nu_{\tau=90} - \nu_{\tau=0})} \quad (7)$$

$\Delta E_{\tau=90}$ and $\Delta E_{\tau=0}$ are taken from the calculations of Suzuki and are equal to 2 and 1.4744, in units of $-\beta$, respectively. The reference values of the experimentally determined energies $\nu_{\tau=90}$ and $\nu_{\tau=0}$ are taken as the 0_0^0 transition energies of isopropylbenzene and trans- β -methylstyrene which are 37668.5 and 34585.0 cm^{-1} , respectively, and ν is the 0_0^0 transition energy of AMS, 35063.7 cm^{-1} . Using these values, $\Delta E(-\beta)$ is calculated to be 1.5556. Figure 6 shows the angle τ plotted as a function of ΔE (taken from the tabulated values given by Suzuki). The value $\tau = 31^\circ$ correlates with our calculated value of ΔE . The gas phase value calculated here is almost identical to the calculated value of τ for AMS in solution ($\tau=33^\circ$).

The excited state torsion angle for AMS can then be one of two values, ~ 0 or $\sim 60^\circ$. In analogy to biphenyl,^{10,14} we suggest the first excited state of AMS to be nearly planar, i.e., $\tau \sim 0^\circ$.

V. CONCLUSIONS

The TOFMS of AMS has been presented and analyzed. The ground state torsional angle τ is calculated to be $\sim 31^\circ$. A Franck-Condon analysis yields a displacement $\Delta\tau$ in the excited state of 30° : we suggest this implies a nearly planar AMS in the excited state S_1 . The potential parameters determined from a hindered rotor analysis of the internal torsional motion of AMS

yields ground state parameters $V_2 = 0.0$ and $V_4 = 150.0 \text{ cm}^{-1}$ and excited state parameters of $V_2 = 4867$, $V_4 = -500$ and $V_6 = -80 \text{ cm}^{-1}$ with a reduced rotational constant of $B = 0.444 \text{ cm}^{-1}$.

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TABLE I

 α -Methylstyrene

	Frequency (cm^{-1})	Spacing (cm^{-1})
T_0^0	0.0	
T_0^1	63.6	63.6
T_0^2	127.6	64.0
T_0^3	194.0	66.4
T_0^4	262.0	68.0
T_0^5	330.0	68.0
T_0^6	401.6	71.6
T_0^7	472.1	70.5
T_0^8	543.2	71.1
T_0^9	614.6	71.4
T_0^{10}	687.7	73.1
T_0^{11}	760.0	72.3

TABLE II
Origin Assignment

	0_0^0 Transition (cm^{-1})
α -methylstyrene	35063.7
d_5 - α -methylstyrene	35083.6

TABLE III

***d*₅-*α*-Methylstyrene**

	Frequency (cm ⁻¹)	Spacing (cm ⁻¹)
T ₀ ⁰	0.0	
T ₀ ¹	58.4	58.4
T ₀ ²	119.0	60.6
T ₀ ³	181.4	62.4
T ₀ ⁴	245.0	63.6
T ₀ ⁵	308.2	63.6
T ₀ ⁶	373.3	65.1
T ₀ ⁷	438.3	65.0
T ₀ ⁸	504.3	66.0
T ₀ ⁹	570.8	66.5
T ₀ ¹⁰	639.3	68.5

TABLE IV
Vibrational Mode Assignments

Assignment	Frequencies (cm ⁻¹)		
	α -methylstyrene	d ₅ - α -methylstyrene	styrene*
1 ^o	738.7	722.1	745.8
6 ¹	394.5	341.1	369.5

* The vibrational frequencies for jet-cooled styrene were taken from Syage, J.A., Al-Adel, F. and Zewail, A.H., Chem. Phys. Lett. 103 (1983) 15.

TABLE V
Calculated and Observed Frequencies[†] of the Torsional Motion of
 α -Methylstyrene and d_5 - α -Methylstyrene

	α -methylstyrene		d_5 - α -methylstyrene	
	observed	calculated ^a	observed	calculated ^b
T_0^0	0.0	0.0	0.0	0.0
T_0^1	63.6	63.5	58.4	59.2
T_0^2	127.6	128.6	119.0	119.8
T_0^3	194.0	195.0	181.4	181.6
T_0^4	262.0	262.7	245.0	244.5
T_0^5	330.0	331.5	308.2	308.3
T_0^6	401.6	401.1	373.3	373.1
T_0^7	472.1	471.6	438.3	438.5
T_0^8	543.2	542.9	504.3	504.7
T_0^9	614.6	614.8	570.8	571.4
T_0^{10}	687.7	687.2	639.3	638.8
T_0^{11}	760.0	750.2		

[†] All frequencies in cm^{-1} .

^a Potential parameters; $V_2=4867$, $V_4=-500$, $V_6=-80$ and $B=0.444 \text{ cm}^{-1}$

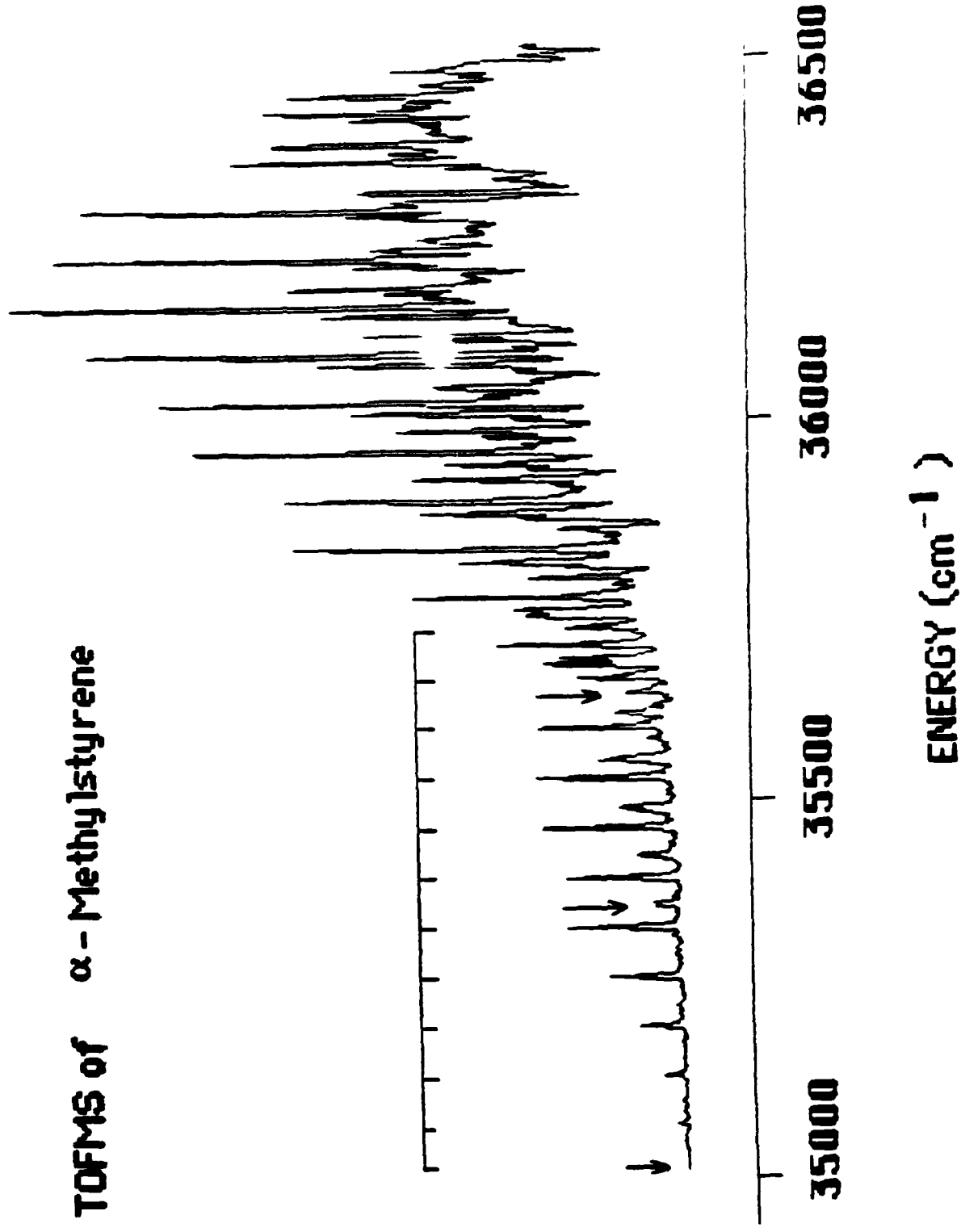
^b Potential parameters; $V_2=4867$, $V_4=-500$, $V_6=-80$ and $B=0.387 \text{ cm}^{-1}$

FIGURE CAPTIONS

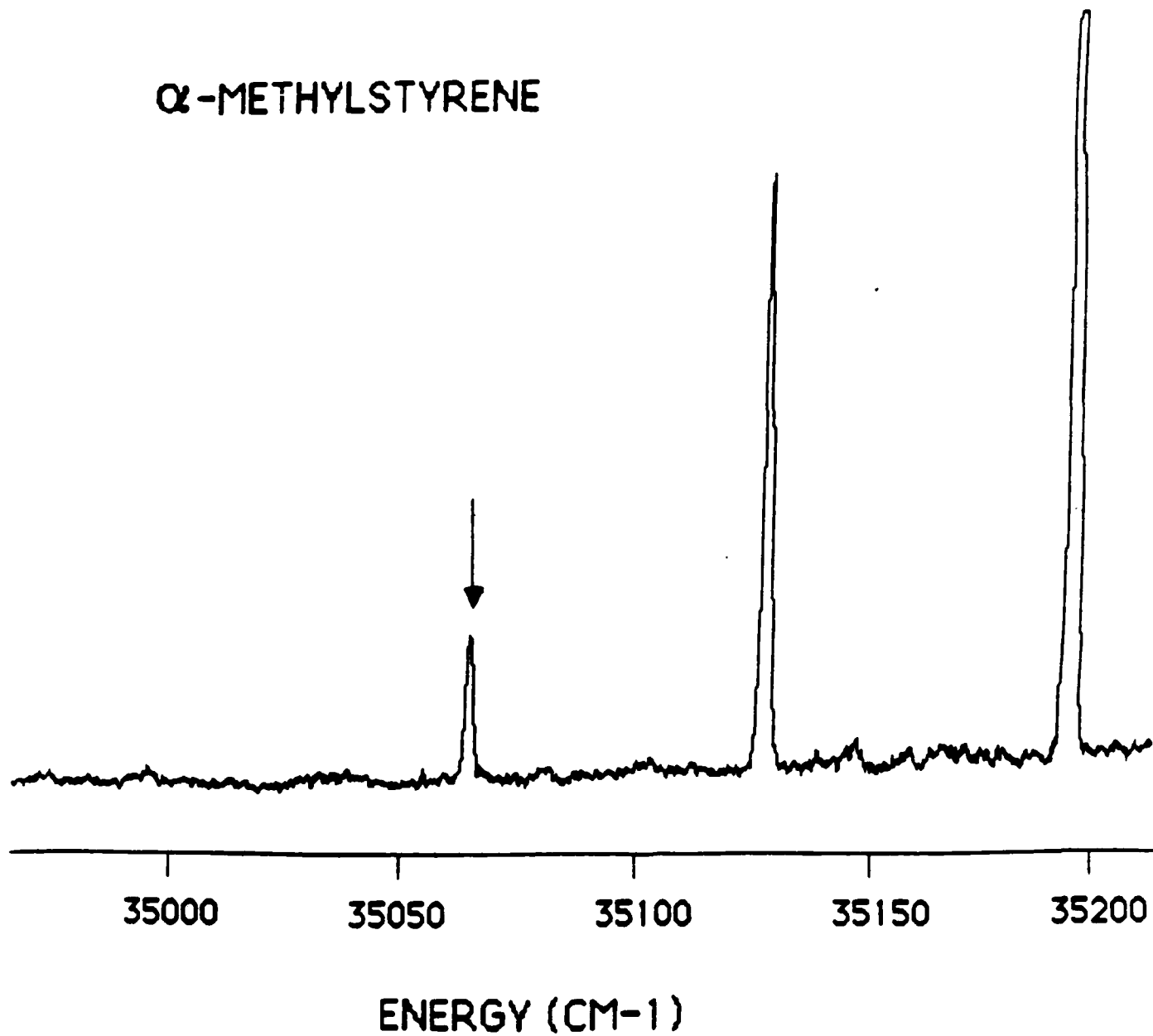
- Figure 1 The TOFMS of α -methylstyrene from ~ 35000 to ~ 36500 cm^{-1} . The origin is very weak in intensity and marked by an arrow. Two other higher vibrational features are also marked by an arrow in the spectrum. A low frequency motion which is built on the origin and higher vibrations is seen in the spectrum with an energy level spacing on the order of 69 cm^{-1} .
- Figure 2 An expanded view of the α -methylstyrene origin region. The origin is identified (arrow) at 35063.7 cm^{-1} . Argon is used as the expansion gas at a pressure of 30 psig.
- Figure 3 The TOFMS of d_5 - α -methylstyrene scanned from 35000 to 36000 cm^{-1} . The origin is marked by an arrow as well as two higher vibrational features. A low frequency mode is seen in the spectrum which has a spacing of ~ 64 cm^{-1} .
- Figure 4 TOFMS of α -methylstyrene at low He expansion pressures. Hot band transitions to the red of the origin are observed for the torsional motion of the propenyl group. The origin transition is at 35063.7 cm^{-1} and therefore not seen in this figure. Similar spectra are observed for the deuterated propenyl group.
- Figure 5 The one-color TOFMS of styrene. The origin region consists solely of an intense peak with no other spectral features up to 200 cm^{-1} . The 0_0^0 transition is at 34778.7 cm^{-1} .

Figure 6 The electronic transition energy plotted as a function of the torsional angle τ for α -methylstyrene, as calculated by Suzuki (see reference 4).

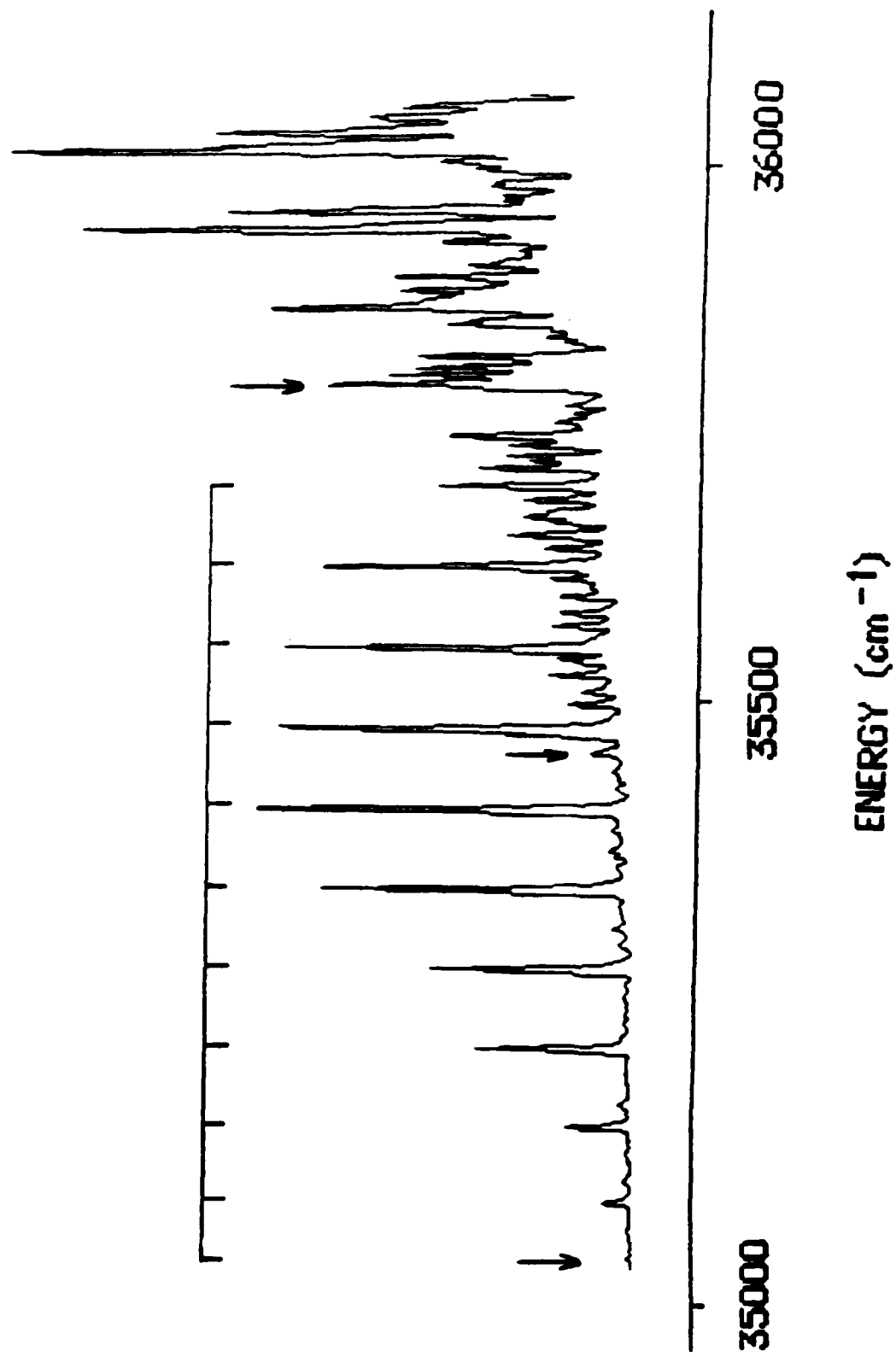
TOFMS of α - Methylstyrene



α -METHYLSTYRENE

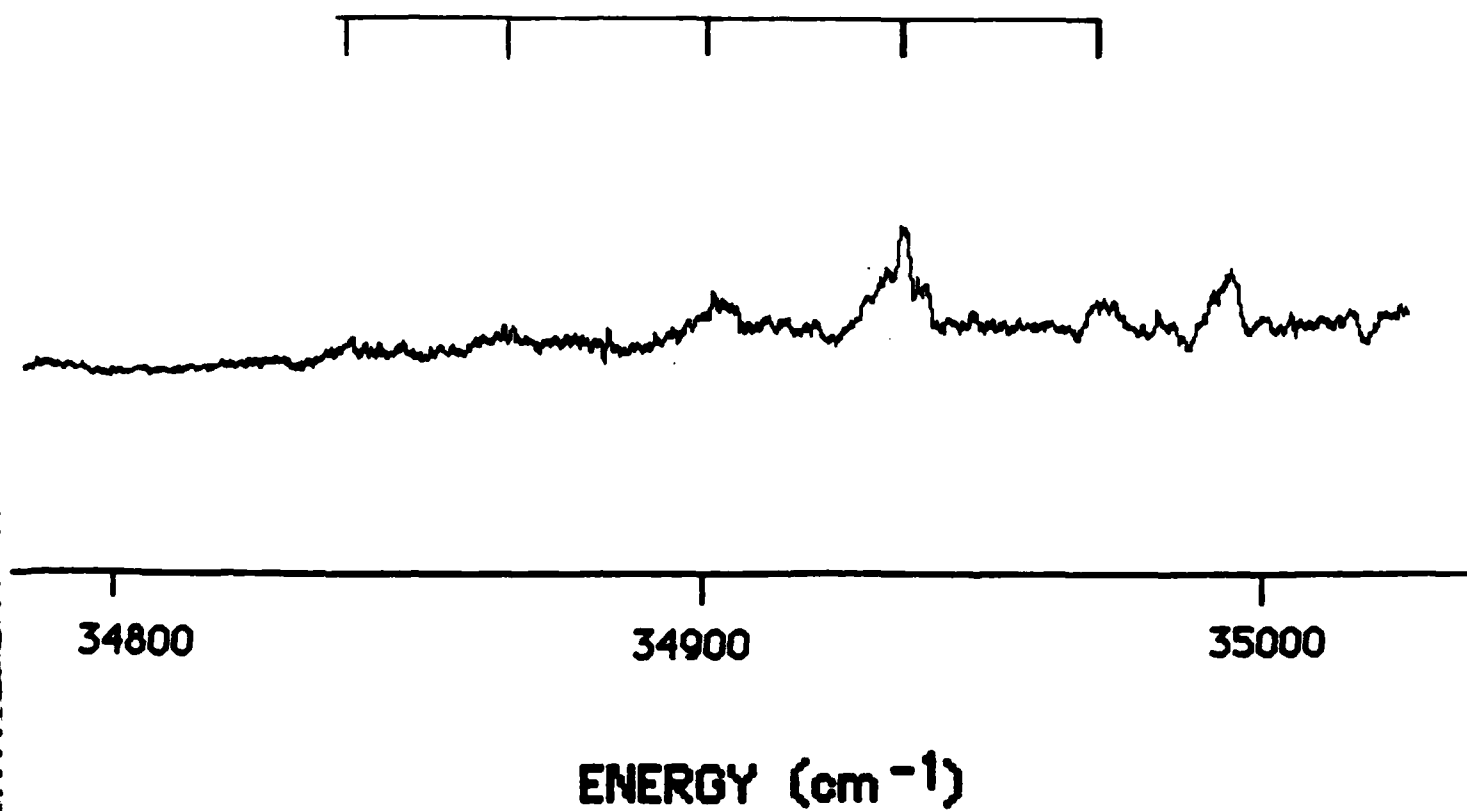


TOFMS of d₅- α -Methylstyrene

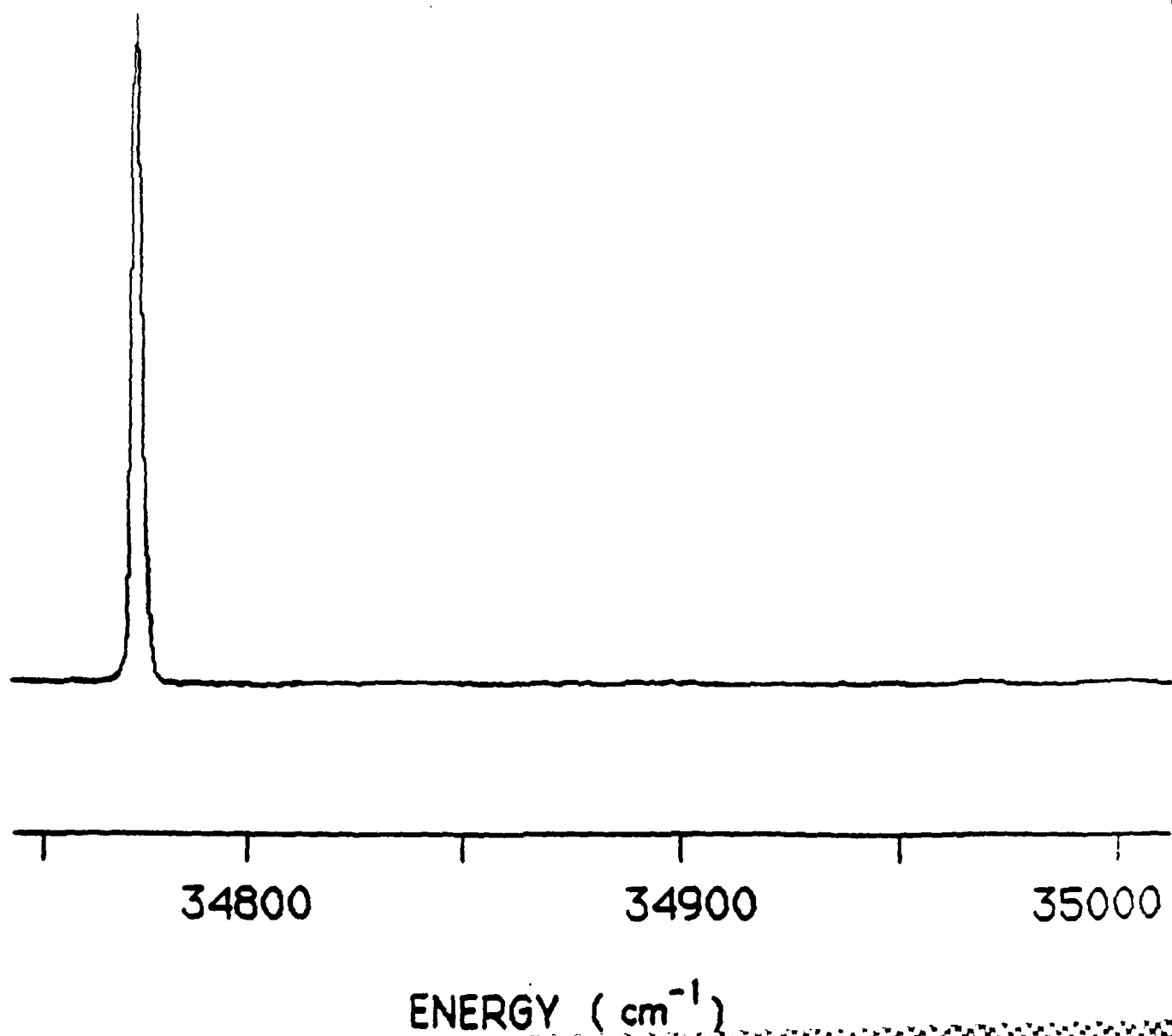


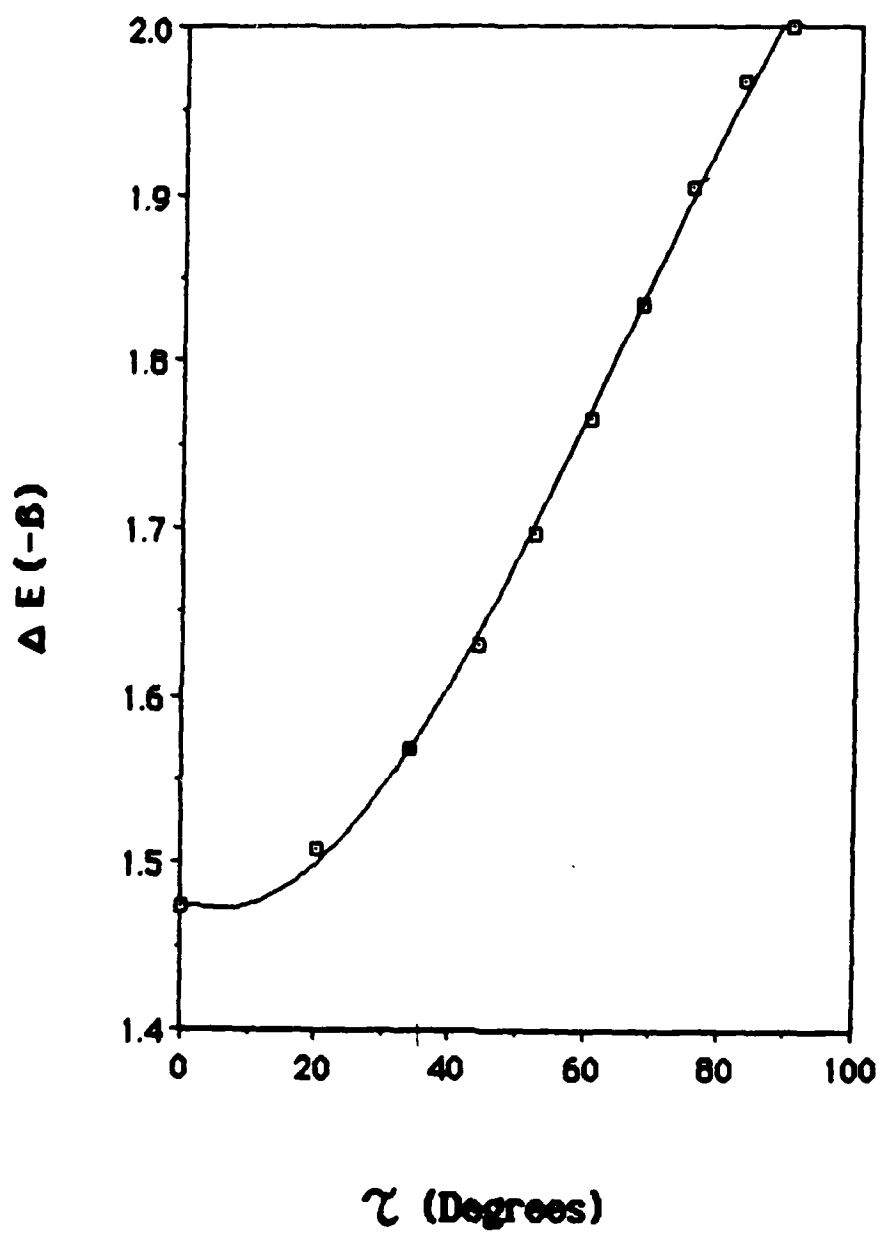
α -Methylstyrene

(P_{He} < 40 psig)



TOFMS of Styrene





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